Appendix K

CLASSES OF CHEMICALS THAT CAN FORM PEROXIDES UPON AGING

Class I: Unsaturated materials, especially those of low molecular weight, may polymerize violently and hazardously due to peroxide initiation.

Acrylic Acid
Acrylonitrile
Butadiene
Chlorobutadiene (chloroprene)
Chlorotrifluoroethylene
Methyl methacrylate
Styrene
Tetrafluoroethylene
Vinyl acetate
Vinyl acetylene
Vinyl chloride
Vinyl pyridine
Vinylidene chloride

Class II: The following are a peroxide hazard upon concentration (distillation/evaporation). A test for peroxide should be performed if concentration is intended or suspected.

Acetal
Cumene
Cyclohexene
Cyclooctene
Cylopentene
Diacetylene
Dicyclopentadiene
Diethylene glycol dimethyl ether
Diethyl ether
Dioxane (*p*-dioxane)
Ethylene glycol dimethyl ether (glyme)
Furan
Methyl acetylene
Methyl cyclopentane
Methyl-*i*-butyl ketone
Tetrahydrofuran
Tetrahydronaphthalene
Vinyl ethers

Class III: Peroxides derived from the following compounds may explode without concentration.

Organic:
Divinyl ether
Divinyl acetylene
Isopropyl ether
Vinylidene chloride

Inorganic:
Potassium metal
Potassium amide
Sodium amide (sodamide)

Reference

National Research Council. Prudent Practices in the Laboratory. National Academy Press, Washington D.C., 1995.

Appendix L

COMMON PEROXIDE-FORMING CHEMICALS

List A: Severe Peroxide Hazard on Storage with Exposure to Air

Discard within three months

Diisopropyl ether (isopropyl ether)
Divinylacetylene (DVA)[1]
Potassium metal
Sodium amide (sodamide)
Vinylidene Chloride (1.1-dichloroethylene)[1]
Potassium amide

List B: Peroxide Hazard on Concentration; Do Not Distill or Evaporate Without First Testing for the Presence of Peroxides

Discard or test for peroxides after six months

Acetaldehyde diethyl acetal (acetal)
Cumene (isopropylbenzene)
Cyclopentene
Cyclopentene
Decalin (decahydronaphthalene)
Dioxane
Ethylene glycol dimethyl ether (glyme)
Ethylene glycol ether acetates
Ethylene glycol monoethers (cellosolves)
Diacetylene (butadiene)
Dicyclopentadiene
Diethyl ether (ether)
Diethylene glycol dimethyl ether (diglyme)
Furan
Methylacetylene
methylcyclopentane
Methyl isobutyl ketone
Tetrahydrofuran (THF)
Tetralin (tetrahydronaphthalene)
Vinyl ethers[1]

List C: Hazard of Rapid Polymerization Initiated by Internally Formed Peroxides[1]

a. *Normal Liquids; Discard or test for peroxides after six months[2]*

Chloroprene (2-chloro-1,3-butadiene)[3]
Styrene
Vinyl acetate
Vinylpyridine

b. Normal Gases; Discard after 12 months[4]

Butadiene[3]
Tetrafluoroethylene (TFE)[3]
Vinylacetylene (MVA)[3]
Vinyl chloride

Appendix L

COMMON PEROXIDE-FORMING CHEMICALS

[1] Polymerizable monomers should be stored with a polymerization inhibitor from which the monomer can be separated by distillation just before use.

[2] Although common acrylic monomers such as acrylonitrile, acrylic acid, ethyl acrylate and methyl methacrylate can form peroxides, they have not been reported to develop hazardous levels in normal use and storage.

[3] The hazard from peroxides in these compounds is substantially greater when they are stored in the liquid phase and if so stored without an inhibitor they should be considered as in LIST A.

[4] Although air will not enter a gas cylinder in which gases are stored under pressure, these gases are sometimes transferred from the original cylinder to another in the laboratory and it is difficult to be sure that there is no residual air in the receiving cylinder. An inhibitor should be put into any such secondary cylinder before one of these gases is transferred into it; the supplier can suggest inhibitors to be used. The hazard posed by these gases is much greater if there is a liquid phase in such a secondary container, and even inhibited gases that have been put into a secondary container under conditions that create a liquid phase should be discarded within 12 months.

References

Jackson, H. L., W. B. McCormack, C. S. Rondesvedt, K. C. Smeltz and I. E. Viele. *Safety in the Chemical Laboratory*. Vol. 3. Easton, PA.

NRC Committee on Hazardous Substances in the Laboratory. *Prudent Practices for Handling Hazardous Chemicals in the Laboratory*. Washington, D.C.: National Academy Press, 1981.

Appendix M

TYPES OF COMPOUNDS KNOWN TO AUTOOXIDIZE TO FORM PEROXIDES

- Aldehydes
- Ethers, especially cyclic ethers and those containing primary and secondary alkyl groups (*never* distill an ether before it has been shown to be free of peroxide)
- Compounds containing benzylic hydrogens
- Compounds containing allylic hydrogens (C=C-CH), including most alkenes; vinyl and vinylidene compounds
- Compounds containing a tertiary C-H group (e.g.), decalin and 2,5-dimethylhexane

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Reference

National Research Council. Prudent Practices in the Laboratory. National Academy Press, Washington, D.C., 1995.